

TITLE

Dimensionally Stable Balloons

CROSS-REFERENCE TO RELATED APPLICATIONS

- 5 This application is a continuation-in-part of copending US Patent Application No. 09/698378 which is a continuation-in-part of US Patent Application No. 09/426384.

BACKGROUND OF THE INVENTION

- 10 Medical catheters having a balloon mounted thereon are useful in a variety of medical procedures. A balloon may be used to widen a vessel into which the catheter is inserted by dilating the blocked vessel, such as in an angioplasty procedure. Some examples of stent delivery balloons are disclosed in U.S. Patent No. 5702418, and U.S. Patent No. 5797877, the entire contents of both patents is hereby incorporated by
- 15 reference. In these and other medical device delivery applications, radial expansion of a balloon may be used to expand or inflate a stent at a desired positioned within the body. Using a balloon equipped catheter to deliver a stent requires precise positioning of the balloon and stent as well as a balloon with accurate and predictable expansion properties. A known drawback of many previous delivery catheters and balloons is that when a
- 20 balloon is radially inflated to a desired extent, the balloon will also expand longitudinally. As a result of longitudinal expansion of a balloon during the delivery of a medical device, the balloon itself, the medical device mounted thereupon or both apparatuses may be shifted from their pre-inflation position resulting in improper delivery of the medical device.
- 25 In balloons where longitudinal expansion occurs, the balloon may expand longitudinally past one or both of the stent ends. Typical stent delivery balloons will expand longitudinally at least 5% beyond the original pre-inflation state. In addition to potentially mis-delivering the medical device as described above, the resulting extended balloon may cause the edges of the stent to push against the vessel wall to a greater
- 30 extent than they would from radial expansion alone.

It has recently been discovered that Liquid Crystal Polymers (LCP) may be effectively blended with other materials and extruded to form high strength medical balloons. In copending U.S. applications 08/926,905 (corresponding to PCT/US98/18345 filed Sept. 4, 1998), and 09/257,677 filed February 25, 1999 there are
5 described medical balloons made from LCP blends. The entire contents of both of these applications is hereby incorporated by reference.

U.S. Patent No. 5,389,314 to Wang discloses an inflatable medical device which has a plurality of longitudinally oriented conduits which extend through out the length of the device. The device may be formed by co-extruding two dissimilar plastic
10 materials. The first material form defining a discrete phase which forms fibers and the other material or continuous phase which forms the remaining balloon material. After extrusion the discrete phase is withdrawn from the continuous phase, leaving the continuous phase with a plurality of conduits therethrough.

15 BRIEF SUMMARY OF THE INVENTION

The present invention is directed generally to medical balloons which expand only to a predetermined extent, and which have minimal longitudinal and/or minimal radial growth during expansion. Specifically, the invention is directed to a stent delivery balloon composed of a micro-composite material which includes a longitudinal
20 fibril structure that is either parallel to the longitudinal axis of the balloon structure, or that is angularly disposed relative to the longitudinal axis at the molecular level of the balloon. The orientation of the fibril structure can limit longitudinal expansion of the balloon and allow the balloon to expand radially as desired, but minimally, or not at all in the longitudinal direction if the fibrils are parallel to the balloon axis, or when the fibrils
25 are oriented diagonally about the axis, can limit both longitudinal and radial expansion of the balloon when inflated.

The micro-composite material is made up of a combination of a fibril component, a semi-compliant balloon material which acts as a matrix, and optionally a compatibilizer material which may act to create a less distinctive phase boundary
30 between the fibril and matrix components, but which does not solubilize the LCP polymer in the matrix at human body temperature.

The present invention provides for a balloon which utilizes LCP materials or other oriented materials such as PET, in combination with a thermoplastic elastomer matrix and an optional compatibilizer to form a micro-composite material. The present micro-composite material is suitable for construction balloons which exhibit minimal or
5 no longitudinal growth during balloon expansion but which expands as desired in the radial direction, or the present micro-composite material is suitable for construction of balloons that exhibit minimal expansion both in the longitudinal and radial directions.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

10 A detailed description of the invention is hereinafter described with specific reference being made to the drawings in which:

FIG. 1 is a schematic representation of side view of a tubular parison used to produce a balloon of the invention from a the micro-fiber composite material;

FIG. 2 is a schematic side view of a medical device delivery balloon
15 constructed from micro-composite material shown at nominal diameter wherein the fibril component is oriented parallel to the longitudinal balloon axis;

FIG. 3 is a view of the medical device delivery balloon shown in Fig. 2 in an inflated state at a pressure higher which causes radial growth of the balloon;

FIG. 4 is a cross-sectional view of a tubular parison for producing balloon
20 of an alternative embodiment of the invention;

FIG. 5 is a perspective view of the embodiment shown in FIG. 4;

FIG. 6 is perspective view of a dilatation balloon preform in a tubular parison form constructed from micro-composite material wherein the inner and outer fibril components have been oriented diagonally to the longitudinal axis of the tubular
25 preform and in crossing relationship relative to each other by use of a counter-rotating extrusion die;

FIG. 7 is another perspective view of only the outer surface of a dilatation balloon preform constructed from micro-composite material wherein the fibril
30 component is oriented diagonally to the longitudinal axis of the tubular preform by use of a rotating die;

FIG. 8 is a schematic side-view of a blow molded dilatation balloon constructed from micro-composite material depicting the fibril component oriented diagonally to the longitudinal axis of the balloon;

Figure 9 is a side view of a parison for producing a balloon of an
5 alternative balloon of the invention;

Figure 10 is a side view of a balloon produced from a parison as in Fig. 9, shown at nominally inflated diameter;

Figure 11 is a view as in Fig 9, shown at a diameter expanded beyond nominal diameter; and

10 Figure 12 is a cross-sectional view of a further alternate embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

While this invention may be embodied in many different forms, there are
15 shown in the drawings and described in detail herein specific preferred embodiments of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated.

As noted above, the present invention relates to medical catheters which
20 have one or more balloon portions constructed from a specially configured micro-composite material. The particular micro-composite material and configuration provides physical properties which allow a balloon to expand radially to a predetermined extent, but which allow only minimal, or more preferably, no longitudinal growth during expansion. The micro-composite material includes a longitudinal fibril component
25 which exhibits micro-fibers in combination with a matrix of any semi-compliant balloon material. Depending on the specific fibril component, as well as the method of extrusion utilized to extrude the balloon material, the micro-fibers may be randomly scattered through out the balloon material or may be precisely spaced about the balloon and extending through the entire balloon length. The fibril structure is oriented or directed in
30 the longitudinal direction of the balloon providing the balloon with desirable radial expansion characteristics and minimal longitudinal growth when the balloon is inflated.

As shown in Fig. 1, the balloons of the invention may be made from tubular parisons 10 of the micro-composite material, having a fibril component which exhibits micro-fibers 12 uniformly oriented in a predetermined direction. In a preferred embodiment shown in Fig. 2, the micro-composite is formed into a balloon 20 from a parison 10 by a conventional balloon blowing process. Balloon 20 has a diameter D and a length L. Micro-fibers 12 are oriented along and about the longitudinal axis 22 of the balloon. The fibril component may be any rigid-rod or semi-rigid-rod thermoplastic material which comprises 0.1 to about 25 percent, and more preferably from about 0.5 to about 20 percent by weight of the micro-composite material. Examples of suitable materials which could be utilized as the fibril component include: liquid crystal polymers such as VECTRA[®] LKX 1107, 1111, polyetheretherketone (PEEK) material, and PPS. Other materials may also be utilized as the fibril component of the present invention. Such substances include aromatic nylon, rigid polyurethane, polyester, copolyester, polyester blends, polyester/polyurethane blends, PEEK, PPS, fluoropolymer and so on.

The diameter of the fiber 12 may be 0.01 micron or larger, and may have a thickness substantially equal to the balloon. The length of the fiber 12 may range from as small as 0.02 microns to being substantially the same length of the balloon.

To form the micro-composite material, the fibril component is preferably combined with a semi-compliant thermoplastic polymer material in a melt blend which at least partially phase separates upon cooling. Under appropriate conditions the phase separated material will form fibrils or micro-fiber 12 embedded in a matrix of the semi-compliant thermoplastic polymer, oriented substantially parallel to the longitudinal axis of the extruded tubing. The micro-composite material suitably employs an amount of semi-compliant polymer matrix component from about 50 to 99.9 percent by weight, preferably from about 85 to 99.5 percent.

Some examples of suitable materials which may be utilized as the matrix component are polyamide-polyether block copolymers, namely the polyamide/polyether/polyesters PEBAX[®] 6333, 7033 and 7233; also polyester-polyether block copolymer such as ARNITEL[®] EM740.

As previously described, the present invention achieves the desired balloon expansion characteristics as a result of forming a balloon composed of a micro-

composite material. The micro-composite material balloon is formed by coextrusion of a melt blend of LCP or other orientable material, the matrix component, and optionally a compatibilizer. A dual extrusion process utilizing two extruders may also be used to form the desired tube. The shear rate at die exit can be in the range of about 200 sec⁻¹, to
5 about 1500 sec⁻¹. Where LCP is used as the fibril component, the shear rate may be about 400 sec⁻¹ to about 1000 sec⁻¹. If the LCP is not subjected to a sufficient shearing force, the LCP will form droplet shaped deposits which provide minimal or no longitudinal stabilization.

If, during extrusion, relative rotation of the mandrel and die is avoided,
10 the fibrils will adopt an orientation substantially parallel to the longitudinal axis. If the die and mandrel are relatively rotated, e/g. by rotation of one or the other or both, the orientation of the fibrils will be helically about the axis.

A balloon which has an LCP fibril component tends to have individual fibers spread randomly throughout the balloon material. The individual LCP fibers will
15 typically be between 0.01 micron to 10 microns in diameter.

If the various components utilized to form the micro-composite material are incompatible to a substantial degree, phase separation may be so efficient that slippage between phases might occur during balloon expansion thereby reducing the longitudinal restriction effect of the fibrils. To prevent such occurrences a compatibilizer
20 may also be desirable for the purpose of enhancing the homogeneity of the melt blend prior to extrusion and cooling. A compatibilizer material may be added to the pre-extruded melt blend material to create a less distinctive phase boundary between the fibril and matrix components. The compatibilizer may be for instance a block copolymer comprising a block which is structurally similar or otherwise is soluble in the matrix
25 polymer and a block which is structurally similar or otherwise soluble with the fibril component.

The compatibilizers include copolyester elastomers; ethylene unsaturated ester copolymers, such as ethylene-maleic anhydride copolymers; copolymers of ethylene and a carboxylic acid or acid derivative, such as ethylene-methyl acrylate copolymers;
30 polyolefins or ethylene-unsaturated ester copolymers grafted with functional monomers, such as ethylene-methyl acrylate copolymers; copolymers of ethylene and a carboxylic

acid or acid derivative, such as ethylene-methyl acrylate-maleic anhydride terpolymers; terpolymers of ethylene, unsaturated ester and a carboxylic acid or acid derivative, such as ethylene-methyl acrylate-methacrylic acid terpolymers; maleic acid grafted styrene-ethylene-butadiene-styrene block copolymers; and acrylic elastomers, such as acrylic rubbers. Similar polymers containing epoxy functional groups, for instance derived from glycidyl methylacrylate, in particular, alkyl (meth)acrylate-ethylene-glycidyl (meth)acrylate polymers can also be usefully employed. Ionomeric copolymers can be employed as compatibilizers. Specific suitable compatibilizers include the copolyester elastomer, Hytrel™ HTR-6108 (DuPont); the ethylene-maleic anhydride copolymer, Polybond™3009 (BP Chemicals); the ethylene-methyl acrylate copolymer, SP 2205 (Chevron); the ethylene-methyl acrylate copolymer grafted with maleic anhydride, DS 1328/60 (Chevron); the ethylene-methyl acrylate-maleic anhydride terpolymer, Lotader™ 2400; the ethylene-methyl acrylate-maleic acid terpolymers, Escor™ ATX-320, Escor™ ATX-325 or Escor™ XV-11.04; the acrylic rubber, Vamac™ G1 and the ethylene-ethyl acrylate-glycidyl methacrylate terpolymer, Lotader™ AX 8660.

A compatibilizer may be employed in an amount from 0 to about 30 weight percent of the total composition.

The balloon 20, shown in Fig. 2 at nominal diameter, is shown in Fig. 3 inflated at a higher pressure which provides radial expansion to a new, larger diameter D'. In the most preferred embodiment, the micro-composite material 10 allows balloon 20 to obtain semi-compliant expansion in the radial direction with reduced balloon expansion in the longitudinal direction during inflation (balloon length L is substantially unchanged in Fig. 3). In some embodiments, longitudinal expansion is less than 10 percent, typically less than 8 percent and in some embodiments less than 6 percent from nominal. Depending on the precise mixture and type of matrix and fibril components used, other embodiments of the present invention may provide for balloons with varying degrees and types of radial expansion while also reducing longitudinal expansion by varying degrees.

If substances less prone to phase separation from the matrix material are desired to be used, an appropriately shaped die may be used in the extrusion process to provide individually extruded fibers evenly around the tube circumference, for instance

in the manner of US 5,389,314 except that the fiber material is selected to adhere to the matrix material and a high line speed is used to provide a microscopic fiber diameter. For such an embodiment, the individual non-LCP fibers may be between about 5 - 20 microns and in particular embodiments may be between about 10-12 microns in diameter
5 and may also extend through the entire length of the balloon in chain or cores.

This embodiment is depicted by the tubular parisons in Figs. 4 and 5. As shown, cores 30 are suspended through out the parison 31 in a matrix 32 which may be composed of any material suitable for constructing a semi-compliant balloon as have been described above. The cores 30 are composed of a material which has a more
10 limited ability to stretch than the matrix material, and when the cores are collectively oriented in the same direction, the structures exhibit an increased longitudinal stability when inflated beyond initial or nominal diameter.

In selecting appropriate materials for the fibrils of cores 30 and matrix 32 it is important to select materials which provide adequate adhesion to one another. If
15 adhesion is insufficient between the cores 30 and the surrounding matrix 32 longitudinal growth of the balloon produced from parison 31 will not be restricted as the more expansive matrix material may slip past the individual cores. A further important attribute of the cores 30 is the bulk elongation of the material. The bulk elongation of the cores 30 is typically less than that of the matrix 32. In preferred embodiments the bulk
20 elongation of the cores 30 may be 200% or less and in some embodiments may be 150% or less. In order to avoid core breakage prior to balloon bursting, it is desirable that if the material from which the cores are constructed exhibit a higher tensile strength than the material of which the matrix is constructed.

Figures 6-8 pertain to alternative embodiments in which the fibers of the
25 balloon are orientated diagonally relative to the longitudinal axis of the balloon. In Figure 6 there is depicted a parison 60 for a balloon in which, in addition to using a high puller speed during extrusion, a counter rotating die was used. The counter rotating die has a mandrel which rotates in one direction and a concentric outer die which rotates in the opposite direction, the parison is extruded through the space between the two. The
30 resulting parison has fibers 62 orientated diagonally to the parison axis 64 in one direction at the outside surface (angle α) and changing gradually as one passes through

the material in a direction transverse to the axis 64 to a second direction (angle β) at the inside surface, the angles determined by outer die/mandrel rotation speeds and puller speed. The angles α and β may be about 0 degrees to about 90 degrees, in some embodiment the angles α and β may be about 15 degrees to about 75 degrees, and in 5 some embodiments the angles α and β may be about 30 to about 60 degrees. If one or the other of the outer die or the mandrel are held stationary while the other is rotated, angle α or angle β may be parallel to the axis 64.

In Figure 7 there is depicted a parison 70, having diagonally oriented fibers formed by relative rotation of the die and puller. For instance only the outer die or 10 mandrel may be rotated so that the fibers become orientated at angle α throughout the entire thickness of the parison.

Figure 8 depicts the outer surface orientation of a balloon 80 made from a parison of either Fig. 6 or Fig 7. In the balloon body the fibers retain an angular orientation relative to the balloon axis and provide resistance to both longitudinal and 15 radial expansion beyond the nominal or molded dimensions.

Angular or helical orientation can also be provided in a modification of the extruded fiber core reinforced balloons of Figures 4 and 5. Instead of orientating the cores 30 parallel to the axis of the parison, as shown in Figure 5, the cores may be extruded as helical coils embedded in the matrix polymer material. Figure 9 depicts such 20 a parison 90 in which the spiraling core fibers are depicted by phantom lines 92. The parison of figure 9 has a cross-section as in Figure 4. Parison 90 may be produced rotating by the die which produces the core fibers 92. Another way to achieve the spiral structure is to rotate the tubing after it exits the die. For instance, a center mandrel which produces the lumen 94 may be rotated to twist the extrusion as it exits the die 25 orifices. As with previous embodiments the core fibers 92 may have a higher tensile strength and lower bulk elongation than the surrounding matrix material 96.

Helical fiber orientations, i.e. fibers which extend longitudinally, but from side view are diagonally disposed to the tube axis, produce balloons which can achieve hinged balloon distention curves. Angular orientation of the fibers in the parison 30 produces a balloon 100 with angular orientation in the balloon body as shown by Figure 10 where some of the fibers 102 are shown by the phantom lines. At a first inflated

diameter, for instance the nominal diameter depicted in Figure 10, the fibers form an angle γ relative to the longitudinal axis. As the balloon is further expanded, the fiber orientation angle increases to a greater angle ϵ , shown in Figure 11. The closer the fiber orientation angle comes to a perpendicular orientation the greater the resistance they provide to further diameter growth and radial expansion. The balloon of Figure 8 behaves in a similar manner.

Advantages for balloons employed in angioplasty, stent placement and other medical applications of "hinged" growth profiles, in which the balloon initially grows at a relatively rapid rate but at higher pressures grows more slowly, have been recognized previously in angioplasty and stent delivery applications. A relatively high growth rate at lower pressures allows the balloon to be used at a larger range of diameters, while the slow rate of growth at high pressure reduces risk of dissection when a high pressure is required to accomplish a lesion dilatation or a firm stent placement. The present invention provides a method for producing a controlled growth profile as desired simply by controlling an extrusion extraction rate and/or rotation factor.

In a still further embodiment of the invention the fibers, whether parallel or helically oriented relative to the parison axis, may be incorporated into one or more layers of a multilayer parison. Figure 12 depicts a cross-section of a three layer parison 110 produced by co-extrusion which has an intermediate layer 112 with embedded reinforcing core fibers 113, and respective inner and outer layers 114, 116 which are free of fiber reinforcement. The fibers 113 may be longitudinally or helically disposed around the longitudinal axis of the parison. Alternative embodiments of such structures include two-layer structures with the fibers on the inner or the outer layer, or both layers but at different orientations; three layer or more layer structures with two or more fiber-containing layers, and embodiments in which, in some or all of the fiber-containing layers, the fibers are oriented microfibers such as LCP fibers oriented in the manner of any of Figs 1, 6 or 7.

In preferred embodiments of a multi-layer balloon there can be from 7 to about 50, preferably from about 9 to about 15, total polymer layers alternating between (A) fiber-free compliant or semi-compliant polymer, for instance a block copolymer comprising polyamide blocks and polyether blocks such as PEBAX[®] 7033 or 7233, or a

polyamide such as nylon 12, or nylon 6, and (B) blends of the same polymer with about 5-50% by weight, more preferably approximately 10-20 % by weight, of an LCP polymer, such as VECTRA® LKX 1111. The ratio A/B of the total thickness of the two types of layers, respectively, being from about 5 to about 15, more preferably about 8-10.

5 A = 50-95%; preferred at 90%; B = 5-50%, preferred at 10%.

Based on the above description it should be understood that several different polymers with a wide range of characteristics may be used to form a longitudinal or longitudinal and radial stabilized balloon of the present invention. The invention is further illustrated by the following non-limiting examples.

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Example 1:

A matrix component of PEBAX® 7033 was mixed with a fibril component of LCP VECTRA LKX 1107 at the ratio of 95% to 5% respectively by weight. The mixture was extruded at a rate of 110 feet/minute line speed into tubing of
15 0.039 (outer diameter) x 0.027 (inner diameter) inch. A 3.5 mm balloon was formed from the resulting tubing by radial expansion at 110 degrees Celsius with blowing pressure of 350 psi. The balloon with double wall thickness of 0.0014 inch was inflated from 4 atm to 13 atm at 1 atm increment and no measurable balloon length change was observed.

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Example 2:

Coextruded 13 layer parisons 0.019 x 0.034 inches were prepared with alternating A & B layers, the A-layers being PEBAX® 7233, the B-layers being PEBAX® 7233 blended with 15% by weight VECTRA® LKX 1111. The parisons were extruded
25 30 at 221°C Balloons of 3.0 mm diameter, 0.00155 inches double wall thickness, were blown. The ETO sterilized balloons had the following characteristics:

Hinged compliance:

ave. growth rate, 3-9 atm - 0.045 mm/atm

ave. growth rate, 12-18 atm - 0.020 mm/atm

30 Diameter change at nominal pressure after balloon inflated to 18 atm - 5.3%

Burst pressure - 26-27 atm

Burst Strength - 23201 psi

Longitudinal growth 12 atm to 18 atm - 5.9%

Example 3:

5 Two extruders are utilized to extrude a plurality of stripes 113 over a metal core. The parison 110 is rotated in one direction with the core at 2000 rpm to produce the helically oriented tubing, such as may be seen in Figs. 9-12. The core fibers 113 may be MXD6 aromatic nylon from Mitsubishi Gas Chemical. The tubing material, such as layers 112, 114 and 116 may be one or more base polymer materials such as 10 PEBAX[®] 7233. The stripes 113 are evenly distributed along the circumference of the tubing and located at the middle of the tubing wall.

In the present example, a 3.0 mm balloon was formed from a tube having an internal diameter of 0.021 inches and an outer diameter of 0.037 inches at 95°C and at 400psi pressure. The balloon burst at 311 psi with double wall thickness of 0.00145 15 inch. The balloon length change was 2.3 percent from 6 atm to 12 atm, and 3.2 percent from 12 to 18 atm.

For comparison purposes in regard to Example 3, tubing of 100 percent PEBAX[®] 7233, with dimensions of 0.0348 (outer diameter) x 0.0200 (inner diameter), is used to form a 3.0 mm balloon at 95°C at 400psi blowing pressure. The formed balloon 20 with double wall thickness of 0.00140 inches burst at 353 psi. The balloon length change was 3.5 percent from 6 atm to 12 atm, and 5.5 percent from 12 to 18 atm.

The above examples and disclosure are intended to be illustrative and not exhaustive. These examples and description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are 25 intended to be included within the scope of the claims, where the term "comprising" means "including, but not limited to". Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims. Further, the particular features presented in the dependent claims can be combined with each other in other manners within the scope 30 of the invention such that the invention should be recognized as also specifically directed to other embodiments having any other possible combination of the features of the

dependent claims. For instance, for purposes of claim publication, any dependent claim which follows should be taken as alternatively written in a multiple dependent form from all prior claims which possess all antecedents referenced in such dependent claim if such multiple dependent format is an accepted format within the jurisdiction (e.g. each claim
5 depending directly from claim 1 should be alternatively taken as depending from all previous claims). In jurisdictions where multiple dependent claim formats are restricted, the following dependent claims should each be also taken as alternatively written in each single dependent claim format which creates a dependency from a prior antecedent-possessing claim other than the specific claim listed in such dependent claim below (e.g.
10 claim 6 may be taken as alternatively dependent from any of claims 2-5, claim 4 may be taken as alternatively dependent from claim 3; etc.).